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(54) Title: LIQUID CLEANING PRODUCTS

(57) Abstract

A substantially non-aqueous liquid cleaning composition comprises a particulate solid phase suspended in a non-aqueous liquid phase. The solid phase includes clay material at a level of from 0.01 to 5 % by weight of the composition, said clay material consisting of platelets having an average largest dimension of less than 1 μm .

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LIQUID CLEANING PRODUCTS

The present invention relates to substantially non-aqueous liquid cleaning products, for example detergent compositions. Non-aqueous liquid products are those containing little or no water.

In liquid cleaning products in general, especially those for the washing of fabrics, it is often desired to suspend particulate solids, which have beneficial auxiliary effects in the wash, for example detersity builders to counteract water hardness, as well as bleaches. To keep the solids in suspension and/or to prevent clear layer separation, generally some sort of stabilising system is necessary.

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It has been proposed in GB 1 205 711 to incorporate highly voluminous metal and metalloid oxides in non-aqueous built liquid detergent compositions. These create a suspending filamentary network of oxide particles.

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As will be explained in more detail hereinbelow, the present invention is founded upon a discovery that non-aqueous liquid detergent compositions with a reduced tendency to clear layer separation can be formulated by including therein a specific kind of clay stabilizer.

It has previously been proposed, for example in EP-A-266 199, to incorporate fabric softening clays in non-aqueous liquid detergent compositions. These fabric softening clays do generally not act as stabilising materials.

US-A-4 264 466 describes liquid mulls having improved physical stability comprising a specific chain structure type clay, such as sepiotlite, attapulgite and palygorskite clays. A disadvantage of using chain structure type clay materials is however that they often lead to undesired viscosity increases of the liquid detergent composition. Comparative example E in column 35 discloses a composition that comprises Veegum T, a hectorite clay. Patentee

indicates that this composition has a poor stability. As indicated in column 34 lines 45-47, the clay was only mixed, which leads to the clay particles having an average largest dimension of more than 1 μm .

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GB-A-2 210 382 discloses the use of cationically modified smectite clay materials in non-aqueous liquid detergent compositions, and on page 34 line 2 Veegum F and Laponite SP are mentioned. However, as indicated on page 41 line 31-32, 10 the particle size of the clay material is 1 μm or larger, preferably 4 to 8 μm . Moreover, the clay material is modified with a quaternary ammonium compound. Such a modification of the clay materials requires an extra 15 processing step which leads to an undesired complication of the process and to an increase in costs. Use of similar clays is disclosed in GB-A-2 208 168.

EP-A-120 659 suggests the use of certain clays such as kaolin, montmorillonites and sodium bentonite as builder 20 materials in non-aqueous liquid detergent products. The average largest dimension of the particles of these clays are all larger than 1 μm . Moreover, use of clay at relatively high levels for providing building properties is often less 25 advantageous because it may cause undesired viscosity increases.

Surprisingly, it has now been found that the stability of non-aqueous liquid detergent compositions comprising a dispersed solid phase can be increased and/or the clear- 30 layer formation of such compositions can be decreased if low levels of clay materials consisting of small platelets are included.

Accordingly, the present invention provides a substantially 35 non-aqueous liquid cleaning product composition comprising a particulate solid phase suspended in a non-aqueous liquid phase, wherein the solid phase includes of from 0.01 to 5% by weight of clay material platelets having an average largest dimension of less than 1 μm .

THE CLAY MATERIAL

Compositions according to the invention comprise from 0.01 to 5% by weight of a clay material, preferably Saponite and/or Hectorite, consisting of platelets having an average 5 largest dimension of less than 1 μm .

Because of their relatively small particle size, preferably synthetic clay materials are used. Particularly preferred are Hectorite clays and especially preferred is the use of 10 Laponite clays, which are synthetic clay materials of the Hectorite type.

Preferably the level of clay material is from 0.02 to 4%, more preferably 0.1 from to 3%, and in any event, most 15 preferably not more than 2% by weight of the composition.

The clay material can be a synthetic clay material or a natural clay material. Preferably for processing reasons unmodified clay material is used, that is, the material has 20 not been treated in such a way as to change its chemical structure.

In compositions in accordance to the invention, any clay material can be used which consists of particles having a 25 platelet shape. The platelet structure of the clay particles can easily be detected by microscopic techniques, for example by electron microscopy. The largest dimension of the platelets is on average less than 1 μm , more preferred from 0.02 to 0.8 μm , most preferred from 0.1 to 0.3 μm , 30 especially preferred from 0.15 to 0.25 μm . These are typical sizes which may be obtained by milling of the compositions, especially ball milling. This is especially advantageous as it avoids producing fine dust which would be formed if the clay were dry milled.

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The average value can be determined by any suitable technique for the determination of particle sizes, most preferably, however the average length of the largest dimension of the particles is determined by electron

microscopy using a number counting method. In the context of the present invention, the term "average" refers to the D(3,2) average.

5 PRODUCT FORM

All compositions according to the present invention are liquid cleaning products. In the context of this specification, all references to liquids refer to materials which are liquid at 25°C at atmospheric pressure. They may 10 be formulated in a very wide range of specific forms, according to the intended use. They may be formulated as cleaners for hard surfaces (with or without abrasive) or as agents for warewashing (cleaning of dishes, cutlery etc) either by hand or mechanical means, as well as in the form 15 of specialised cleaning products, such as for surgical apparatus or artificial dentures, paint removal compositions and compositions for cleaning metals. They may also be formulated as agents for washing and/or conditioning of fabrics.

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Thus, the compositions will contain at least one agent which promotes the cleaning and/or conditioning of the article(s) in question, selected according to the intended application. Usually, this agent will be selected from surfactants, 25 enzymes, bleaches, microbiocides, (for fabrics) fabric softening agents and (in the case of hard surface cleaning) abrasives. Of course in many cases, more than one of these agents will be present, as well as other ingredients commonly used in the relevant product form.

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Preferably the viscosity of compositions in accordance to the invention is less than 2,500 mPa.s at 21 s⁻¹, more preferably between 50 and 2,000, most preferably from 300 to 1,500.

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SURFACTANT

Where surfactants are solids, they will usually be dissolved or dispersed in the liquid phase. Where they are liquids, they will usually constitute all or part of the liquid

phase. However, in some cases the surfactants may undergo a phase change in the composition.

In general, surfactants for use in the compositions of the

5 invention may be chosen from any of the classes, sub-classes and specific materials described in "Surface Active Agents" Vol. I, by Schwartz & Perry, Interscience 1949 and "Surface Active Agents" Vol. II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's

10 Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in "Tensid-Taschenbuch", H. Stache, 2nd Edn., Carl Hanser Verlag, München & Wien, 1981.

15 In respect of all surfactant materials, but also with reference to all ingredients described herein as examples of components in compositions according to the present invention, unless the context requires otherwise, the term "alkyl" refers to a straight or branched alkyl moiety having

20 from 1 to 30 carbon atoms, whereas lower alkyl refers to a straight or branched alkyl moiety of from 1 to 4 carbon atoms. These definitions apply to alkyl species however incorporated (e.g. as part of an aralkyl species). Alkenyl (olefin) and alkynyl (acetylene) species are to be

25 interpreted likewise (i.e. in terms of configuration and number of carbon atoms) as are equivalent alkylene, alkenylene and alkynylene linkages. For the avoidance of doubt, any reference to lower alkyl or C_{1-4} alkyl (unless the context so forbids) is to be taken specifically as a

30 recitation of each species wherein the alkyl group is (independent of any other alkyl group which may be present in the same molecule) methyl, ethyl, iso-propyl, n-propyl, n-butyl, iso-butyl and t-butyl, and lower (or C_{1-4}) alkylene is to be construed likewise.

35 Preferably the total level of surfactants is from 5-75 % by weight of the composition, more preferably 15-60 %, most preferably 25-50 %.

NON-IONIC SURFACTANTS

Nonionic detergent surfactants are well-known in the art.

They normally consist of a water-solubilizing polyalkoxylene or a mono- or di-alkanolamide group in chemical combination

5 with an organic hydrophobic group derived, for example, from alkylphenols in which the alkyl group contains from about 6 to about 12 carbon atoms, dialkylphenols in which each alkyl group contains from 6 to 12 carbon atoms, primary, secondary or tertiary aliphatic alcohols (or alkyl-capped derivatives 10 thereof), preferably having from 8 to 20 carbon atoms, monocarboxylic acids having from 10 to about 24 carbon atoms in the alkyl group and polyoxypropylenes.

Also common are fatty acid mono- and dialkanolamides in

15 which the alkyl group of the fatty acid radical contains from 10 to about 20 carbon atoms and the alkyloyl group having from 1 to 3 carbon atoms. In any of the mono- and di-alkanolamide derivatives, optionally, there may be a 20 polyoxyalkylene moiety joining the latter groups and the hydrophobic part of the molecule.

In all polyalkoxylene containing surfactants, the polyalkoxylene moiety preferably consists of from 2 to 20 groups of ethylene oxide or of ethylene oxide and propylene oxide groups. Amongst the latter class, particularly 25 preferred are those described in the applicants' published European specification EP-A-225,654, especially for use as all or part of the liquid phase.

30 Also preferred are those ethoxylated nonionics which are the condensation products of fatty alcohols with from 9 to 15 carbon atoms condensed with from 3 to 11 moles of ethylene oxide. Examples of these are the condensation products of C11-13 alcohols with (say) 3 to 7 moles of ethylene oxide. 35 These may be used as the sole nonionic surfactants or in combination with those of the described in the last-mentioned European specification, especially as all or part of the liquid phase.

Another class of suitable nonionics comprise the alkyl polysaccharides (polyglycosides/oligosaccharides) such as described in any of specifications US 3,640,998; US 3,346,558; US 4,223,129; EP-A-92,355; EP-A-99,183; EP 5 70,074, '75, '76, '77; EP 75,994, '95, '96.

Mixtures of different nonionic detergent surfactants may also be used. Mixtures of nonionic detergent surfactants with other detergent surfactants such as anionic, cationic 10 or amphotolytic detergent surfactants and soaps may also be used. Preferably the level of nonionic surfactants is from 5-75 % by weight of the composition, more preferably 15-60%, most preferably 25-50%.

15 ANIONIC SURFACTANTS

Examples of suitable anionic detergent surfactants are alkali metal, ammonium or alkylolamine salts of alkylbenzene sulphonates having from 10 to 18 carbon atoms in the alkyl group, alkyl and alkylether sulphates having from 10 to 24 20 carbon atoms in the alkyl group (especially branched alkyl sulphates), the alkylether sulphates having from 1 to 5 ethylene oxide groups, and olefin sulphonates prepared by sulphonation of C10-24 alpha-olefins and subsequent neutralization and hydrolysis of the sulphonation reaction 25 product.

All ingredients before incorporation will either be liquid, in which case, in the composition they will constitute all or part of the liquid phase, or they will be solids, in 30 which case, in the composition they will either be dispersed in the liquid phase or they will be dissolved therein. Thus as used herein, the term "solids" is to be construed as referring to materials in the solid phase which are added to the composition and are dispersed therein in solid form, 35 those solids which dissolve in the liquid phase and those in the liquid phase which solidify (undergo a phase change) in the composition, wherein they are then dispersed.

THE NON-AQUEOUS ORGANIC SOLVENT

As a general rule, the most suitable liquids to choose as the liquid phase are those organic materials having polar molecules. In particular, those comprising a relatively 5 lipophilic part and a relatively hydrophilic part, especially a hydrophilic part rich in electron lone pairs, tend to be well suited. This is completely in accordance with the observation that liquid surfactants, especially polyalkoxylated nonionics, are one preferred class of 10 material for the liquid phase.

Non-surfactants which are suitable for use as the liquid phase include those having the preferred molecular forms referred to above although other kinds may be used, 15 especially if combined with those of the former, more preferred types. In general, the non-surfactant solvents can be used alone or with in combination with liquid surfactants. Non-surfactant solvents which have molecular structures which fall into the former, more preferred 20 category include ethers, polyethers, alkylamines and fatty amines, (especially di- and tri-alkyl- and/or fatty- N-substituted amines), alkyl (or fatty) amides and mono- and di- N-alkyl substituted derivatives thereof, alkyl (or fatty) carboxylic acid lower alkyl esters, ketones, 25 aldehydes, and glycerides. Specific examples include respectively, di-alkyl ethers, polyethylene glycols, alkyl ketones (such as acetone) and glyceryl trialkylcarboxylates (such as glyceryl tri-acetate), glycerol, propylene glycol, and sorbitol.

30

Many light solvents with little or no hydrophilic character are in most systems, unsuitable on their own Examples of these are lower alcohols, such as ethanol, or higher alcohols, such as dodecanol, as well as alkanes and olefins. 35 However, they can be combined with other liquid materials.

PROPORTION OF LIQUID PHASE

The liquid phase (whether or not comprising liquid surfactant) in an amount of at least 10% by weight of the

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total composition. The amount of the liquid phase present in the composition may be as high as about 90%, but in most cases the practical amount will lie between 20 and 70% and preferably between 35 and 50% by weight of the composition.

5

SOLIDS CONTENT

In general, the solids content of the product may be within a very wide range, for example from 10-90%, usually from 30-80% and preferably from 50-65% by weight of the final 10 composition. The solid phase should be in particulate form and have an average particle size of less than 300 μm , preferably less than 200 μm , more preferably less than 100 μm , especially less than 10 μm . The particle size may even 15 be of sub-micron size. The proper particle size can be obtained by using materials of the "appropriate size or by milling the total product in a suitable milling apparatus. In order to control aggregation of the solid phase leading to unredispersible settling or setting of the composition, it is preferred to include a deflocculant therein.

20

OTHER INGREDIENTS

In addition to the components already discussed, there are very many other ingredients which can be incorporated in liquid cleaning products.

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There is a very great range of such other ingredients and these will be chosen according to the intended use of the product. However, the greatest diversity is found in products for fabrics washing and/or conditioning. Many 30 ingredients intended for that purpose will also find application in products for other applications (e.g. in hard surface cleaners and warewashing liquids).

DETERGENCY BUILDERS

35 The detergency builders are those materials which counteract the effects of calcium, or other ion, water hardness, either by precipitation or by an ion sequestering effect. They comprise both inorganic and organic builders. They may also be sub-divided into the phosphorus-containing and non-

phosphorus types, the latter being preferred when environmental considerations are important.

In general, the inorganic builders comprise the various 5 phosphate-, carbonate-, silicate-, borate- and aluminosilicates-type materials, particularly the alkali-metal salt forms. Mixtures of these may also be used.

Examples of phosphorus-containing inorganic builders, when 10 present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates.

15 Examples of non-phosphorus-containing inorganic builders, when present, include water-soluble alkali metal carbonates, bicarbonates, borates, silicates, metasilicates, and crystalline and amorphous aluminosilicates. Specific 20 examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

Examples of organic builders include the alkali metal, 25 ammonium and substituted ammonium, citrates, succinates, malonates, fatty acid sulphonates, carboxymethoxy succinates, ammonium polyacetates, carboxylates, polycarboxylates, aminopolycarboxylates, polyacetyl carboxylates and polyhydroxsulphonates. Specific examples 30 include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid. Other examples are organic phosphonate type sequestering agents such as 35 those sold by Monsanto under the tradename of the Dequest range and alkanehydroxy phosphonates.

Other suitable organic builders include the higher molecular weight polymers and co-polymers known to have builder

properties, for example appropriate polyacrylic acid, polymaleic acid and polyacrylic/ polymaleic acid co-polymers and their salts, such as those sold by BASF under the Sokalan Trade Mark.

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Preferably the level of builder materials is from 1 to 40% by weight of the composition, more preferably 5-40% by weight.

10 THE DEFLOCCULANT

Preferably compositions of the invention also comprise a deflocculant material. In principle, any material may be used as a deflocculant provided it fulfills the deflocculation test described in European Patent Specification EP-A-266199 (Unilever). The capability of a substance to act as a deflocculant will partly depend on the solids/liquid phase combination. However, especially preferred are acids.

15 "Fatty" anions are very suitable deflocculants, and a particularly preferred class of deflocculants comprises anionic surfactants. Although anionics which are salts of alkali or other metals may be used, particularly preferred are the free acid forms of these surfactants (wherein the metal cation is replaced by an H⁺ cation, i.e. proton). These anionic surfactants include all those classes, sub-classes and specific forms described in the aforementioned general references on surfactants, viz, Schwartz & Perry, Schwartz Perry and Berch, McCutcheon's, Tensid-Taschenbuch; 20 and the free acid forms thereof. Many anionic surfactants have already been described hereinbefore. In the role of deflocculants, the free acid forms of these are generally preferred.

25 30 35 In particular, some preferred sub-classes and examples are the C10-C22 fatty acids and dimers thereof, the C8-C18 alkylbenzene sulphonic acids, the C10-C18 alkyl- or alkylether sulphuric acid monoesters, the C12-C18 paraffin sulphonic acids, the fatty acid sulphonic acids, the

benzene-, toluene-, xylene- and cumene sulphonic acids and so on. Particularly are the linear C12-C18 alkylbenzene sulphonic acids.

- 5 As well as anionic surfactants, zwitterionic-types can also be used as deflocculants. These may be any described in the aforementioned general surfactant references. One example is lecithin.
- 10 The level of the deflocculant material in the composition can be optimised by the means described in the aforementioned EP-A-266199, but in very many cases is at least 0.01%, usually 0.1% and preferably at least 1% by weight, and may be as high as 15% by weight. For most 15 practical purposes, the amount ranges from 2-12%, preferably from 4-10% by weight, based on the final composition.

THE BLEACH SYSTEM

Bleaches include the halogen, particularly chlorine bleaches 20 such as are provided in the form of alkalinmetal hypohalites, e.g. hypochlorites. In the application of fabrics washing, the oxygen bleaches are preferred, for example in the form of an inorganic persalt, preferably with a bleach precursor, or as a peroxy acid compound.

- 25 In the case of the inorganic persalt bleaches, the activator makes the bleaching more effective at lower temperatures, i.e. in the range from ambient temperature to about 60°C, so that such bleach systems are commonly known as low- 30 temperature bleach systems and are well-known in the art. The inorganic persalt such as sodium perborate, both the monohydrate and the tetrahydrate, acts to release active oxygen in solution, and the activator is usually an organic compound having one or more reactive acyl residues, which 35 cause the formation of peracids, the latter providing for a more effective bleaching action at lower temperatures than the peroxybleach compound alone.

The ratio by weight of the peroxybleach compound to the

activator is from about 20:1 to about 2:1, preferably from about 10:1 to about 3.5:1. Whilst the amount of the bleach system, i.e. peroxybleach compound and activator, may be varied between about 5% and about 35% by weight of the total liquid, it is preferred to use from about 6% to about 30% of the ingredients forming the bleach system. Thus, the preferred level of the peroxybleach compound in the composition is between about 5.5% and about 27% by weight, while the preferred level of the activator is between about 0.5% and about 14%, most preferably between about 1% and about 10% by weight.

Typical examples of the suitable peroxybleach compounds are alkali metal perborates, both tetrahydrates and monohydrates, alkali metal percarbonates, persilicates and perphosphates, of which sodium perborate is preferred.

It is particularly preferred to include in the compositions, a stabilizer for the bleach or bleach system, for example ethylene diamine tetramethylene phosphonate and diethylene triamine pentamethylene phosphonate or other appropriate organic phosphonate or salt thereof, such as the Dequest range hereinbefore described. These stabilisers can be used in acid or salt form, such as the calcium, magnesium, zinc or aluminium salt form. The stabilizer may be present at a level of up to about 1% by weight, preferably between about 0.1% and about 0.5% by weight.

The applicants have also found that liquid bleach precursors, such as glycerol triacetate and ethylidene heptanoate acetate, isopropenyl acetate and the like, also function suitably as a material for the liquid phase, thus obviating or reducing any need of additional relatively volatile solvents, such as the lower alkanols, paraffins, glycols and glycoethers and the like, e.g. for viscosity control.

MISCELLANEOUS OTHER INGREDIENTS

Other ingredients comprise those remaining ingredients which may be used in liquid cleaning products, such as fabric

conditioning agents, enzymes, perfumes (including deoperfumes), micro-biocides, colouring agents, fluoresces, soil-suspending agents (anti-redeposition agents), corrosion inhibitors, enzyme stabilising agents, and lather 5 depressants.

Amongst the fabric conditioning agents which may be used, either in fabric washing liquids or in rinse conditioners, are fabric softening materials, quaternary ammonium salts, imidazolinium salts, fatty amines and cellulases.

10

Enzymes which can be used in liquids according to the present invention include proteolytic enzymes, amylolytic enzymes and lipolytic enzymes (lipases). Various types of proteolytic enzymes and amylolytic enzymes are known in the 15 art and are commercially available. They may be incorporated as "prills" "marumes" or suspensions e.g.

The fluorescent agents which can be used in the liquid cleaning products according to the invention are well known 20 and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in a detergent composition is generally from 25 0.02-2% by weight.

When it is desired to include anti-redeposition agents in the liquid cleaning products, the amount thereof is normally from about 0.1% to about 5% by weight, preferably from about 30 0.2% to about 2.5% by weight of the total liquid composition. Preferred anti-redeposition agents include carboxy derivatives of sugars and celluloses, e.g. sodium carboxymethyl cellulose, anionic poly-electrolytes, especially polymeric aliphatic carboxylates, or organic 35 phosphonates.

WATER

The compositions are substantially non-aqueous, i.e. they contain little or no free water, preferably no more than 5%,

preferably less than 3%, especially less than 1% by weight of the total composition. It has been found that the higher the water content, the more likely it is for the viscosity to be too high, or even for setting to occur.

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USE

Composition in accordance with the present invention may be used for several detergency purposes, for example the cleaning of surfaces and the washing of fabrics. For the 10 washing of fabrics, preferably an aqueous liquor containing 0.1 to 10 %, more preferably 0.2 to 2%, of the non-aqueous detergent composition of the invention is used.

PROCESSING

15 During manufacture, it is preferred that all raw materials should be dry and (in the case of hydratable salts) in a low hydration state, e.g. anhydrous phosphate builder, sodium perborate monohydrate and dry calcite abrasive, where these are employed in the composition. In a preferred process, the 20 dry, substantially anhydrous solids are blended with the liquid phase in a dry vessel. If deflocculant materials are used, these should preferably -at least partly- be mixed with the liquid phase, prior to the addition of the solids. In order to minimise the rate of sedimentation of the 25 solids, this blend is passed through a grinding mill or a combination of mills, e.g. a colloid mill, a corundum disc mill, a horizontal or vertical agitated ball mill, to achieve a particle size of 0.1 to 100 μm , preferably 0.5 to 50 μm , ideally 1 to 10 μm . A preferred combination of such 30 mills is a colloid mill followed by a horizontal ball mill since these can be operated under the conditions required to provide a narrow size distribution in the final product. Of course particulate material already having the desired particle size need not be subjected to this procedure and if 35 desired, can be incorporated during a later stage of processing.

During this milling procedure, the energy input results in a temperature rise in the product and the liberation of air

entrapped in or between the particles of the solid ingredients. It is therefore highly desirable to mix any heat sensitive ingredients into the product after the milling stage and a subsequent cooling step. It may also be 5 desirable to de-aerate the product before addition of these (usually minor) ingredients and optionally, at any other stage of the process. Typical ingredients which might be added at this stage are perfumes and enzymes, but might also include highly temperature sensitive bleach components or 10 volatile solvent components which may be desirable in the final composition. However, it is especially preferred that volatile material be introduced after any step of de-aeration. Suitable equipment for cooling (e.g. heat exchangers) and de-aeration will be known to those skilled 15 in the art.

For ensuring that the clay material consist of platelet shaped particles of the desired particle size it is preferred to mix the clay materials into the compositions 20 under high shear conditions, preferably before the milling step.

It follows that all equipment used in this process should preferably be completely dry, special care being taken after 25 any cleaning operations. The same is true for subsequent storage and packing equipment.

Example 1

The following compositions (percent by weight) were prepared by mixing the ingredients in the order stated. The ingredients were milled after mixing to give a weight
 5 average particle size of 5 μm .

	<u>Ingredient (% wt)</u>	<u>Composition</u>	
		<u>A</u>	<u>B</u>
	Nonionic (1)	31.996	42.9
10	GTA	15.0	6.1
	Dodecyl benzene sulphonic (free) acid	6.0	3.4
	Na carbonate	18.0	15.8
	Calcite (Sokal U3)	7.0	7.6
15	Clay (2)	1.0	1.7
	Silica (Sipernat D17)	2.0	3.4
	Na Perborate monohydrate	10.5	11.0
	TAED	3.0	3.4
	SCMC	1.0	-
20	Fluorescer	0.3	-
	Versa TL3 polymer	0.5	-
	Methylhydroxyethyl cellulose	0.5	-
	Silicone oil antifoam	2.0	2.0
	Protease	0.4	0.4
25	Lipolase	0.3	0.3
	Perfume	0.5	0.5
	Colour	0.004	0.1

Both compositions were of surprisingly good stability.
 30 Composition A yielded a clear layer separation of 2.0 mm whilst composition B produced 3.0 mm. In both cases, the total sample height was 16 cm. These results were achieved upon storage at 37°C for 4 weeks. The viscosity of composition A was 917 mPas and of composition B was 880
 35 mPas, both measured at a shear rate of 21s⁻¹.

Example 2

		<u>% weight</u>
	Nonionic (1)	19.55
	Nonionic (3)	19.55
5	Alf-5 (4)	0.5
	Wax (5)	0.5
	Sodium metasilicate	Y%
	SCMC (6)	1.5
	Dequest 2041 (7)	0.2
10	Blancophor MBBH 766 (8)	0.5
	Sokolan CP-7 (9)	5.0
	Tylose MH-20 (10)	0.5
	Calcium Oxide	1.0
	Clay	X%
15	Perborate monohydrate (sodium salt)	20.0
	minors	0.5

The following viscosities and stabilities were measured as the components of Example 2 were varied:

20	Clear Layer				
	formation on				
	<u>4 weeks 37°C</u>				
	<u>% Additonal</u>				<u>(stability)</u>
	nonionic (1)	mPa.s 21s ⁻¹			
	y%	added on top	viscosity		
22.5	2	0	3574		0.5mm
25	22.5	2	2750		0.5mm
	22.5	2	2011		1.0mm
	22.5	2	1451		2.0mm
	21.5	3	3652		0.5mm
30	21.5	3	1641		1.5mm
	28.0	0	1503		7.0mm
	22.5	0	814		18.0mm

35 (1) A C₁₀-C₁₂ fatty alcohol ethoxylated with an average of 6.5 ethylene oxide groups per molecule ex Vista.
 (2) Laponite, a synthetic hectorite clay having a number average largest dimension as determined by electron microscopy of 0.2 μm , ex Laporte.

- (3) A C₁₃-C₁₅ fatty alcohol ethoxylated with an average of 3¹³ ethylene oxide groups per molecule, ex ICI.
- (4) C₁₈ alkylphosphate ex Lankro
- (5) Wax 'Ter Hell' M.pt. 70°C, ex Paramelt Syntac
- 5 (6) Sodium carboxymethyl cellulose, 4MOF, ex Hercules
- (7) Phosphonate sequestrant, ex Degussa
- (8) ex Bayer
- (9) Copolymer builder, ex BASF
- (10) ex Hoechst

CLAIMS

1. A substantially non-aqueous liquid cleaning product composition comprising a particulate solid phase suspended 5 in a non-aqueous liquid phase, wherein the solid phase includes of from 0.01 to 5% by weight of clay material platelets having an average largest dimension of less than 1 μm .
- 10 2. A composition in accordance to claim 1, wherein the clay material is a synthetic clay material.
3. A composition in accordance to claim 1, wherein the clay material is of the Hectorite-type.
- 15 4. A composition according to any preceding claim, wherein the amount of the clay material is 2% by weight or less.
7. A composition according to any preceding claim, wherein 20 the average largest dimension of the platelets is from 0.02 μm to 0.8 μm .
8. A composition according to any preceding claim, wherein the clay is not modified with a quaternary ammonium 25 compound.
9. A composition according to any preceding claim, wherein the clay is cationically unmodified.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/00997

I. CLASSIFICATION & SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1. 5 C11D3/12; C11D17/00

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.C1. 5	C11D

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	GB,A,2 208 232 (COLGATE PALMOLIVE) 15 March 1989 see page 9, line 28 - page 10, line 19; claims 1,2 see page 31, paragraph 3 ----	1-4
A	EP,A,0 030 096 (ICI) 10 June 1981 see page 2, paragraph 26 -paragraph 27; claims 1,4 ----	1,2
A	EP,A,0 407 187 (UNILEVER) 9 January 1991 see page 4, line 5 - line 30; claims 1-3 ----	1-9
A	EP,A,0 337 219 (HOECHST AG) 18 October 1989 see claims 1,4 ----	1
		-/-

¹⁰ Special categories of cited documents :¹⁰^{"A"} document defining the general state of the art which is not considered to be of particular relevance^{"E"} earlier document but published on or after the international filing date^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)^{"O"} document referring to an oral disclosure, use, exhibition or other means^{"P"} document published prior to the international filing date but later than the priority date claimed^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention^{"X"} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step^{"Y"} document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.^{"&"} document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 22 JULY 1993	Date of Mailing of this International Search Report 13.08.93
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International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

KLER E.K.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 328 182 (PROCTER AND GAMBLE) 16 August 1989 see page 4, line 44 - line 45; claims 1,3 -----	1-9

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9300997
SA 72845

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 22/07/93

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